## Facile Synthesis of Size-Tunable and Monodisperse

## Tin Arsenide Nanocrystals

Electronic Supplementary Information

## **Experimental Section**

**Materials:** Oleylamine (OLA) and 1-octadecene (ODE) were purchased from Acros and TCI America respectively. Tin(IV) iodide (99.998%) was purchased from Alfa Aesar. Tris(dimethylamino)arsine ((As(NMe<sub>2</sub>)<sub>3</sub>), 99%) wt% in hexane) was purchased from Strem Chemicals. OLA and ODE were degassed and dried under vacuum at 120 °C for 2 h. Methanol was dried with molecular sieves and toluene was dried with Na and both solvents were distilled under nitrogen before use. All other chemicals were used in this synthesis and characterization as received without further purification. [Caution:  $(As(NMe_2)_3)$  is pyrophoric and ignites immediately when exposed to air. Therefore, properly trained personnel should only carry out this synthesis under inert-gas conditions.]

**Synthesis of SnAs NCs:** In a typical synthesis of SnAs NCs, stock solutions of As(NMe<sub>2</sub>)<sub>3</sub> /ODE (0.25 mmol of As(NMe<sub>2</sub>)<sub>3</sub> in 2 mL of ODE) was freshly prepared in a nitrogen glovebox. SnI<sub>4</sub> (anhydrous, 0.2 mmol), OLA (6 mL) was taken in a 50 mL three neck flask and degassed at 120 °C for 30 min to form a clear solution. The reaction was flushed with N<sub>2</sub> for at least two times and heated to 250 °C. At this temperature, As(NMe<sub>2</sub>)<sub>3</sub>/ODE stock solution was swiftly injected. Upon injection, the temperature was dropped to 227–232 °C and allowed to heat back to 250 °C to produce cubic SnAs NCs. The reaction was aged for 5 min at 250 °C to form brown color solution. For NCs size tunability, varied growth times (10, 15 and 30 min) were employed. **Isolation and Purification:** After the desired growth time, the reaction was quenched immediately by removing the heating mantle followed by blowing compressed air until the temperature reaches below 100 °C. Then, 5 mL of toluene was injected at ~90 °C. The resulting NCs were precipitated with excess methanol as anti-solvent, followed by centrifugation at 5000g for 10 min. The NCs were purified by re-dispersion in toluene (3–4 mL) and re-precipitation with methanol (~10 mL). The purification process was repeated at least two times to obtain orange-brown color precipitates and were dried under vacuum prior for further characterization.

Characterization: The powder X-ray diffraction (PXRD) patterns were recorded using a Rigaku Multiflex diffractometer equipped with a Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Purified NCs powder was loaded onto zero background sample holders and the diffraction patterns was recorded at 45 kV and 40 mA operating conditions. The cubic SnAs (JCPDS No. 01-089-3403) crystallite sizes were estimated by applying the Scherrer formula<sup>1</sup> to the (200), (220), and (222) reflections. X-ray photoelectron spectroscopy (XPS) studies were performed on a Shimadzu ESCA 3400 spectrometer equipped with an Al Ka source. Powder samples were pressed onto indium foil (Sigma-Aldrich) prior to analysis. Sample surface charging was corrected to adventitious carbon and peak fits were performed with Themo Advantage software, utilizing a simple Gauss-Lorentz (GL) product function with smart background selection. The IR spectra of NPs were recorded on a Nicolet 670 FT-IR instrument equipped with a single reflection diamond ATR attachment. Carl Zeiss model Ultra 55 scanning electron microscope (SEM) coupled with an energy dispersive spectroscopy (EDS) unit operating at 20 keV was employed for elemental analysis. Low resolution transmission electron microscopy (LRTEM) images were recorded on a JEM-2100 (JEOL) microscope operating at 120 kV. High resolution transmission electron microscopy (HRTEM) images were recorded on a FEI Titan 8300 microscope equipped with a Gatan 794 multiscan camera operating at 300 kV. Samples for TEM analysis were prepared by drop casting the NPs dispersed in hexane onto carbon coated copper grids, followed by evaporation of the solvent.



**Fig. S1.** A typical NaCl type cubic crystal structure of SnAs (blue: Sn and green: As) with space group of Fm-3m (225). The structure was drawn using VESTA software by taking lattice parameter, a = 5.72513(4) Å and Sn and As at the 4b (1/2, 1/2, 1/2) and 4a (0, 0, 0) sites, respectively.<sup>2</sup>



Fig. S2. A representative TEM image of SnAs NCs with varying growth time; (A) 20 min. ( $6.4 \pm 0.6$  nm) and (B) 25 min. ( $7.2 \pm 0.7$  nm) showing the narrow dispersity. The average particle sizes are shown in parenthesis.

| Samula | Growth time | Atomia % of     | Atomia % of     |
|--------|-------------|-----------------|-----------------|
| Sample | Giowin time | Atomic % 01     | Atomic 70 01    |
|        | (min)       | Sn <sup>a</sup> | As <sup>a</sup> |
| 1      | 5           | 45.7 ± 1.8      | 54.3 ± 1.4      |
| 2      | 10          | $45.8\pm2.3$    | $54.2 \pm 2.1$  |
| 3      | 15          | 47.1 ± 1.6      | $52.9 \pm 1.3$  |
| 4      | 30          | $48.5 \pm 1.9$  | 51.3 ± 1.6      |

**Table S1.** Comparison of the Crystallite Size and Primary Particle Size for Varying ReactionGrowth Times of SnAs NCs.

<sup>a</sup>The average Sn and As atomic ratios obtained in atomic % from at least 5 individual measurements of the same sample.



**Fig. S3**. XPS spectra of (A) O(1s) and (B) N(1s) regions of SnAs NCs produced at 250 °C in OLA/ODE system for 30 min. Black lines are spectral data, red and blue lines are fitted deconvolutions. The peak at 531.2 eV in O(1s) spectrum is due to adsorbed H<sub>2</sub>O on NC surface. N 1s spectra show the presence of N–H and N–Sn bonds with binding energies ~399.2 and 400.5 eV, respectively. The existence of N–H and N–Sn bonds suggest that the NCs are passivated by OLA ligands.

## References

- H. Borchert, E. V. Shevehenko, A. Robert, I. Mekis, A. Kornowski, G. Grubel and H. Weller, *Langmuir*, 2005, 21, 1931-1936.
- Y. Wang, H. Sato, Y. Toda, S. Ueda, H. Hiramatsu, and H. Hosono, *Chem. Mater.* 2014, 26, 7209–7213.